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Nitrocampholactone and
Isonitrocampholactone

Chemistry

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NITROCAMPHOLACTONE AND ISONITROCAMPHOLACTONE

BY

RALPH WALDO TIPPET

B. A. Lawrence College, 1913.

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF ARTS

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1915

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THE GRADUATE SCHOOL

June 1, 1915

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Ralph Waldo Tippet

ENTITLED NITROCAMPHOLACTONE AND ISONITROCAMPHOLACTONE

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ARTS IN CHEMISTRY

Wm A. Noyes
In Charge of Thesis

W. A. Noyes
Head of Department

Recommendation concurred in:*

Committee
on
Final Examination*

*Required for doctor's degree but not for master's.

[illegible]

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Nitrocampholactone

and

Isocampholactone

By

R. W. Tippet

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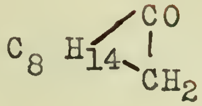
HISTORICAL PART.

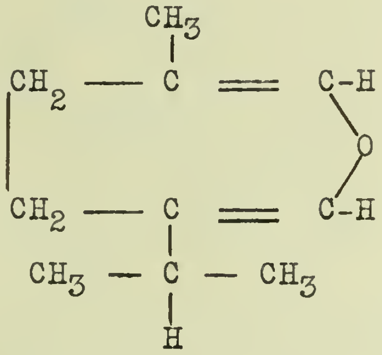
HISTORICAL.[1]

Camphor. 

$$C_8H_{14}\begin{array}{l}\diagup CO \\ \quad | \\ \diagdown CH_2\end{array}$$

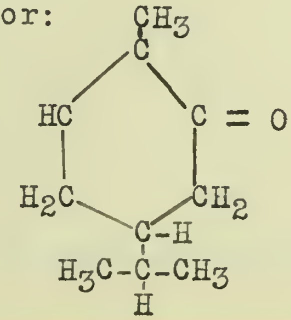
Common or dextro camphor was used for this investigation. It is an opaque, white, wax-like substance melting at 178.4°C. and having a specific rotation of + 44.22°.[1] It was known as far back as the fifth century A.D. when it was thought to be of mineral origin.

Dumas in 1833 showed by analysis that camphor had the composition $C_{10}H_{16}O$. Since that time no less than twenty-five different formulae have been assigned, that of Victor Meyer[2] in 1870 being among the first.

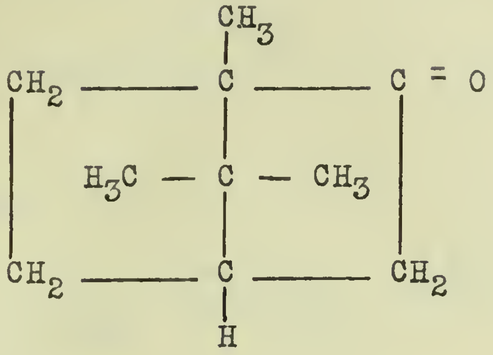


This formula was based on the fact that para cymene was formed from camphor by the loss of water, and that camphoric acid is not a derivative of benzene.

In 1873[3] Kekulé gave the following formula, also based on the formation of para cymene from camphor:

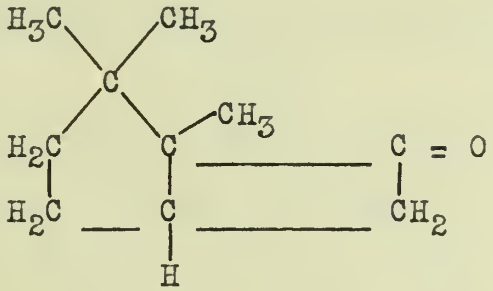


Twenty years later Bredt[4], guessing at the formula of camphoronic acid proposed,



as the formula for camphor.

The occurrence of tri-methyl succinic acid among the oxidation products of camphor, and the supposed proof offered by Walker[5] and Noyes[6], that the two carboxyl groups of camphoric acid are on adjacent carbon atoms, led Bouveault to propose this formula,

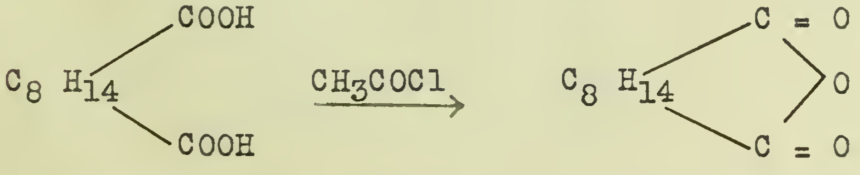


in 1897.

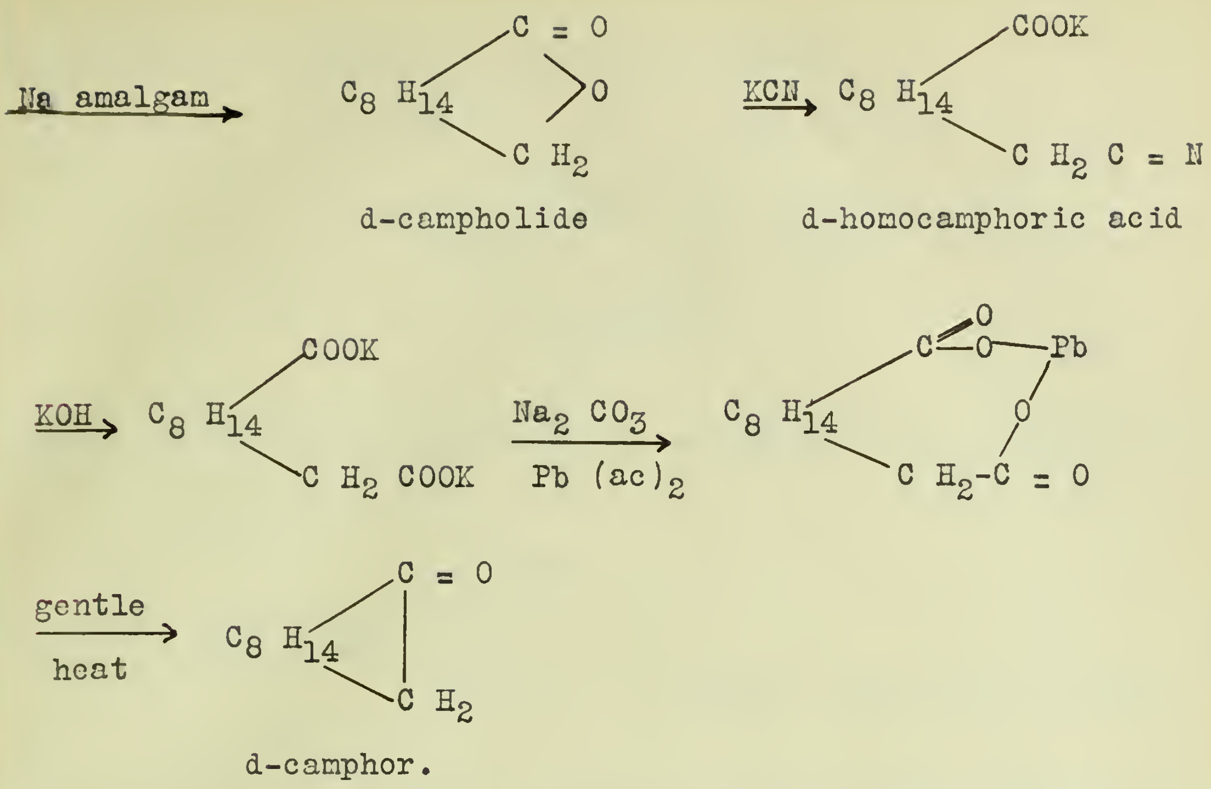
The ease with which the camphor molecule rearranges made it almost impossible to decide between these numerous formulae.

However, in 1903, Komppa[8] synthesized r-camphoric acid and thus proved the correctness of Bredt's[4] second formula for camphor.

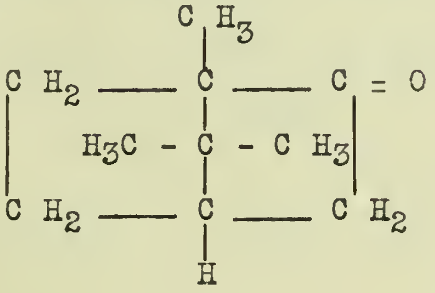
In 1895 Haller[9] synthesized d-camphor from d-camphoric acid as follows:-



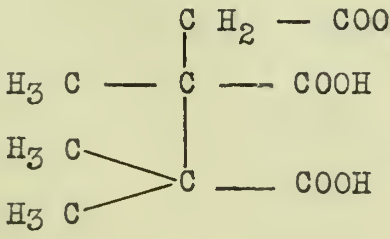
d-camphoric acid d-camphoric anhydride



This synthesis established Bredt's[4] formula which is,

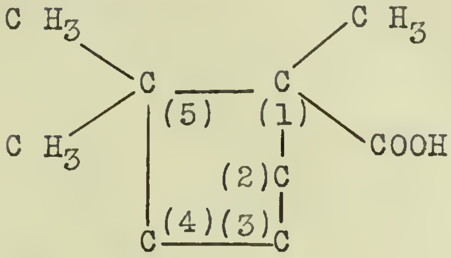


Since camphoric acid is a saturated compound, it must be composed of a ring of carbon atoms, and the only possible arrangement consistent with the formula of camphoronic acid,

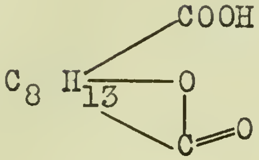
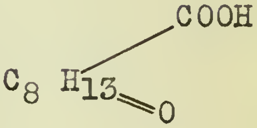


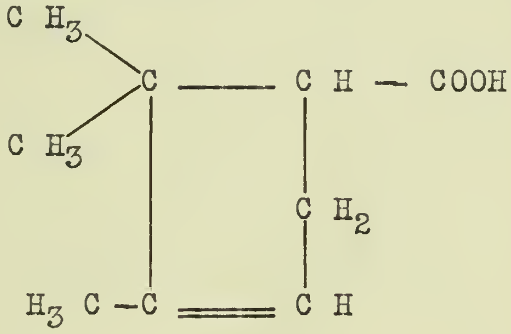
prepared by further oxidation of camphoric acid, and synthetically

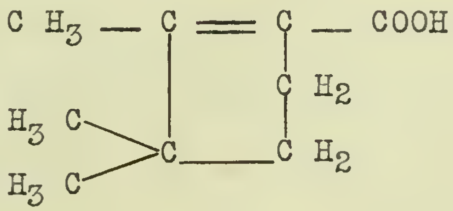
by Perkin, must have as a basis the skeleton,



The second carboxyl group must be attached to the carbon atoms numbered 2, 3, or 4.

Camphanic acid  gives a keto-acid,  which contains the oxygen in place of the carboxyl and hydrogen atoms which are attached to carbon atom 4, since the acid is stable, while if the oxygen were in position 2, the acid would be unstable. This excludes position 2 for the carboxyl group.

a-campholytic acid, 

retains the secondary carboxyl of camphoric acid, and can be converted to b-campholytic acid by,  by warming with dilute acids.

But when a-campholytic acid is reduced to $C_8H_{15}COOH$, and the car-

boxyl and a hydrogen atom of the latter are replaced by oxygen, the resulting cyclic ketone is different from 2, 3-3, -tri-methyl-cyclopentanone prepared from b-campholytic acid. The structure of a-campholytic acid, therefore, which is nearest to that of camphor must be difference from that of b-campholytic acid, to which it can be converted by the simple shifting of the methyl group from one carbon atom to the other and changing the position of the double union[10]. This is only possible in case the second carboxyl group of camphoric acid occupies position 4.

Kosegarten[11], in 1785 first prepared camphoric acid by repeatedly pouring concentrated nitric acid over camphor. Many different methods have been used in preparing camphoric acid, but oxidation by nitric acid has remained the standard method.

In 1840 Schwanert[12] heated camphor with concentrated nitric acid and obtained a better yield. Wreden[13], in 1872, improved the method by using more dilute acid and heating the mixture longer. The best method is that of Noyes[14], 1894. The camphor is heated with dilute nitric acid (Sp.Gr. 1.27) for three days on the steam bath, and the solution allowed to cool. The acid is then filtered, suspended in water, and treated with ammonia till solution is affected. It is then precipitated by the addition of hydrochloric acid. In this manner a yield of 60 per cent of the weight of camphor used is obtained.

In 1885 Woringer[15] prepared lauronolic acid by the distillation of camphoric acid[16]. More recently, Aschan prepared it directly from bromo-camphoric anhydride by treating it with $Na_2 CO_3$, proving that the bromine is in the alpha position. By this method he obtained 160 grams of lauronolic acid from 1 kg. of camphoric acid.

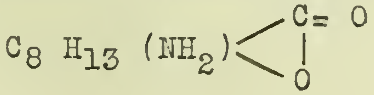
An attempt was made to oxidize lauronolic acid with potassium permanganate, but the products isolated were volatile fatty acids, oxalic acid, some unchanged lauronolic acid, and an acid giving an insoluble lead salt, but in too small an amount for further investigation.

Schryver[16] obtained nitrocampholactone from lauronolic acid by heating it in a reflux condenser with concentrated nitric acid and then pouring into cold water and recrystallizing from absolute alcohol. This lactone has a melting point of $170^{\circ}C$.

A more convenient method for the preparation of nitrocampholactone is one in which lauronolic acid is treated in a shallow dish in small amounts, with nitrogen peroxide formed by heating lead nitrate. The acid first turns green and becomes warm, then loses its color, and on cooling becomes solid, and is then dried on a porous plate, and recrystallized from absolute alcohol.

A small amount of nitrocampholactone was also made by the action of concentrated nitric acid on campholactone when warmed. No action takes place in the cold.

When this compound is exposed to the action of zinc dust and glacial acetic acid, an hydroxylamine derivative is formed, but when reduced with tin and hydrochloric acid, aminocampholactone,



$$C_8H_{13}(NH_2)<\begin{matrix}C=O\\ |\\ O\end{matrix}$$

is formed.

Some work has also been done on the nitro derivative of isocampholactone and its reduction product, aminoisocampholactone[18].

When isocampholactone[19] is heated for three days with nitric acid (Sp.Gr.1.27) in a flask connected with a condenser, it is chiefly converted into nitroisocampholactone. This is separated

by pouring the solution into water, when the lactone precipitates as a white crystalline substance melting at 122°C.

The filtrate, on evaporating leaves an oily residue which crystallizes on standing. After purification this acid melts at 138°C. The barium salt of this acid was prepared by treating with barium carbonate and water.

An imide, $C_3 H_{11} O_2 CONH_2$, was formed by warming 0.5 gram of the acid with an excess of phosphorus pentachloride and then pouring the cooled product into ammonia. The imide melts at 164°C.

The latter part of this paper is a review of the work done in an attempt to prepare an hydroxy acid from camphanic acid, first preparing the silver salt, then the di-ethyl ester, then by saponification the salt, from which the acid should be liberated by the addition of hydrochloride acid.

EXPERIMENTAL PART.

EXPERIMENTAL.

Preparation of Camphoric Acid.

Two hundred grams of camphor are treated with 1500 cc. nitric acid (Sp.Gr.1.42) and 1000 cc. water in a 3-liter flask on the steam bath for three days. The flask is fitted with a loosely fitting stopper to act as a sort of condenser for the volatile camphor. The acid separates on cooling and is then suspended in water, to which ammonia is added until no further solution can be obtained, keeping the mixture cool during the operation.

After filtering, hydrochloric acid is added and the pure camphoric acid is precipitated as a white, heavy mass, which after washing and drying forms a fine, white powder.

The mother liquors from the oxidation may be used twice more by adding enough concentrated nitric acid to bring the specific gravity up to 1.27-1.28. In this manner, 120 grams of the acid are obtained from 200 grams of camphor, melting at 187°C. An 0.08475% solution of this acid in alcohol gives a rotation + 39.6°.

Camphoric Anhydride.

Eighty-two grams of camphoric anhydride were obtained from 100 grams of camphoric acid by treating with acetic anhydride and acetyl chloride, and then pouring into water.

Bromocamphoric anhydride[8].

Fifty grams of camphoric acid treated with 105 grams PCl_5 in a flask are placed on the water bath and warmed until all of the PCl_5 has gone into solution. The flask is then connected with a

reflux condenser and 44 grams of dry bromine added. The heating is continued until the hydrobromic acid has been completely removed, usually requiring 5 or 6 hours. When thoroly cooled it is poured into 6 or 8 volumes of cold water, surrounded by ice and allowed to remain until all the $POCl_3$ is decomposed. The supernatant liquid is poured off and a mixture of 80 grams glacial acetic acid and 20 grams water is added and warmed on the water bath, keeping the temperature below 70°. After heating for an hour, the flask is set aside to cool. The anhydride is then filtered and dried in a vacuum. 46-48 grams were obtained in this manner, melting at 216°.

Camphanic acid[8].

One hundred grams of the above anhydride together with 45 grams of Na_2CO_3 in a 15% solution, were warmed in a flask with an air condenser until solution resulted, generally requiring 8 or 10 hours. After filtering, the solution was treated with 12 grams of sulphuric acid and 50 grams water and distilled with steam. The distillate, after saturating with sodium chloride, was twice extracted with ether, which on evaporating left a few grams of lauronolic acid. An equal volume of hot water was added to the distillation liquor and the whole made acid with sulphuric acid. After standing 12 hours, camphanic acid separated out in long white needles which on drying, fall to a fine white powder, melting at 193°.

Lauronolic Acid[9].

By distilling this acid in an atmosphere of carbon dioxide and heating the vapors to 200°, under reduced pressure, lauronolic

acid and laurolactone are formed. If the CO_2 is not kept in contact with the acid it turns green on heating.

The distillate is distilled with steam when lauronolic acid and laurolactone go over. The watery distillate is taken up with ether and the ethereal solution treated three times with $NaHCO_3$ solution. By this means the sodium salt of lauronolic acid is formed while the lactone is removed in the ether solution. The solution of the salt is made acid with dilute sulphuric and cooled with ice. The lauronolic acid is then extracted with ether. From 50 grams of camphanic acid, 18-20 grams lauronolic acid boiling at 135° at 14 mm were obtained.

Nitrocampholactone[10].

A few grams of lauronolic acid, when exposed to the fumes of nitrogen peroxide formed by heating lead nitrate gave first a bluish green color and then became colorless after about ten minutes and crystallized after cooling. If the NO_2 was kept in contact with the acid longer than ten minutes, the lactone would not crystallize and no crystalline product could be separated from it. The best results were obtained when only a few drops of the acid were treated at a time with the NO_2. The lactone was dried on a porous plate, taken up with alcohol (absolute) and precipitated by the addition of a drop of water. This compound melts at 171°.

An attempt to prepare nitrocampholactone by the direct nitration of campholactone with nitric acid (Sp.Gr.1.27) was unsuccessful. When gently warmed on the water bath, the action was so vigorous as to blow the contents completely out of the tube.

One cubic centimeter of the lactone was added slowly from

a pipette to a mixture of concentrated sulphuric and nitric acids, previously cooled with ice, and pouring the mixture over cracked ice. No nitrated product resulted from this method.

Hydroxyacid.

In the preparation of this acid 0.3 gram of nitrocampholactone was placed in a test tube with 10 cc. N/5 KOH solution and allowed to stand until complete solution, shaking occasionally. After acidifying the solution, it was extracted with ether, dried over Na_2SO_4, and the ether evaporated. The acid weighs 0.21 grams and melted at 124.5^o, after crystallizing from ligroin and benzene. Using the same amounts of the lactone and acid and warming slightly to hasten the reaction, no acid was obtained on evaporation of the ether, showing that decomposition takes place when warmed. The lactone is not completely soluble in cold KOH solution, but dissolves readily when warmed. After standing in KOH solution for 4 days, 0.0007 grams remained undissolved out of 0.3 gram. 0.261 grams lactone in 10 cc. .289/N KOH took 6.5 cc. 0.240 N/HCl to neutralize the solution. This is equivalent to 1.17 moles of KOH reacting with 1 mole of the nitrocampholactone. From this it seems that this is a monobasic acid.

One milligram of the nitrocampholactone ($C_8H_{13}CO_2NO_2$), warmed with 6.92 cc. 0.289/N KOH was titrated with 0.240/N HCl, taking 4.31 cc. using phenolphthalein as indicator. After finding the end point with phenolphthalein, methyl red was used and no change was noted.

One mole of nitrocampholactone reacts with 1.23 mols KOH.

On extraction with ether, the acid formed from the cold

solution gave 0.241 grams, while the solution that was heated gave only 0.03 gram.

Another milligram mole of the nitrolactone dissolved in 20 cc. N/10 KOH in the cold required 3.4 cc. of N/10 HCl to neutralize using phenolphthalein as indicator and then an additional 7.25 cc. using methyl red as indicator. This is equivalent to 0.923 moles of nitrocampholactone for 1 mole of KOH.

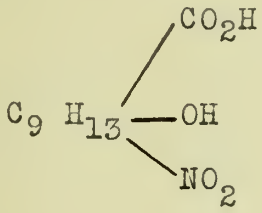
Under the same conditions and using the same amount of the lactone and KOH, 3.2 cc. N/10 HCl were required with phenolphthalein as indicator and 6.9 cc. in addition, with methyl red as indicator 0.987 moles KOH react with 1 mole of the lactone. These results seem to indicate that decomposition has taken place and carbon dioxide has been formed. The mother liquor of this acid gave a qualitative test for nitrous acid, and on analysis, 1 cc. was found to contain 0.002 mg. HNO_2 or 0.0002 per cent.

One tenth (0.1002) gram of the nitrocampholactone were shaken for 4.5 hours with 7 cc. N/10 KOH solution and the undissolved lactone filtered and weighed in a gold crucible. Residue, 0.023 gram. As this residue melts at 168°, no change has taken place. On titrating the solution with N/10 HCl using methyl red as indicator, 5.7 cc. were required. From these results 0.0728 grams KOH reacts with 0.0772 grams of the lactone, giving a possible molecular weight of 522 for the lactone. Titration back with phenolphthalein and N/10 KOH took 1.6 cc. and then again 1.6 cc. HCl, which gives a possible molecular weight of 245 for the lactone. As a check on the previous titrations, I evacuated the solution in a dessicator half an hour over soda lime and sulphuric acid, and again titrated with N/10 KOH and phenolphthalein which took 1.2 cc. N/10 HCl re-

quired 1.2 cc. to neutralize the solution. After evacuating another two hours over soda lime and sulphuric acid 1.1 cc. N/10 KOH were required to neutralize the solution, and finally 1.2 cc. N/10 HCl were required to give the end point with methyl red. After the addition of a slight excess of HCl, the solution was extracted six times with ether as the acid is slightly soluble in water, but no crystalline acid was obtained on evaporation of the ether. The solution from which the acid was extracted, turned brown after standing a few hours. From these results it may be assumed that the lactone has gone into solution without undergoing any decomposition.

Analysis of the acid obtained in the several determinations gave the following results:-

Calculated for

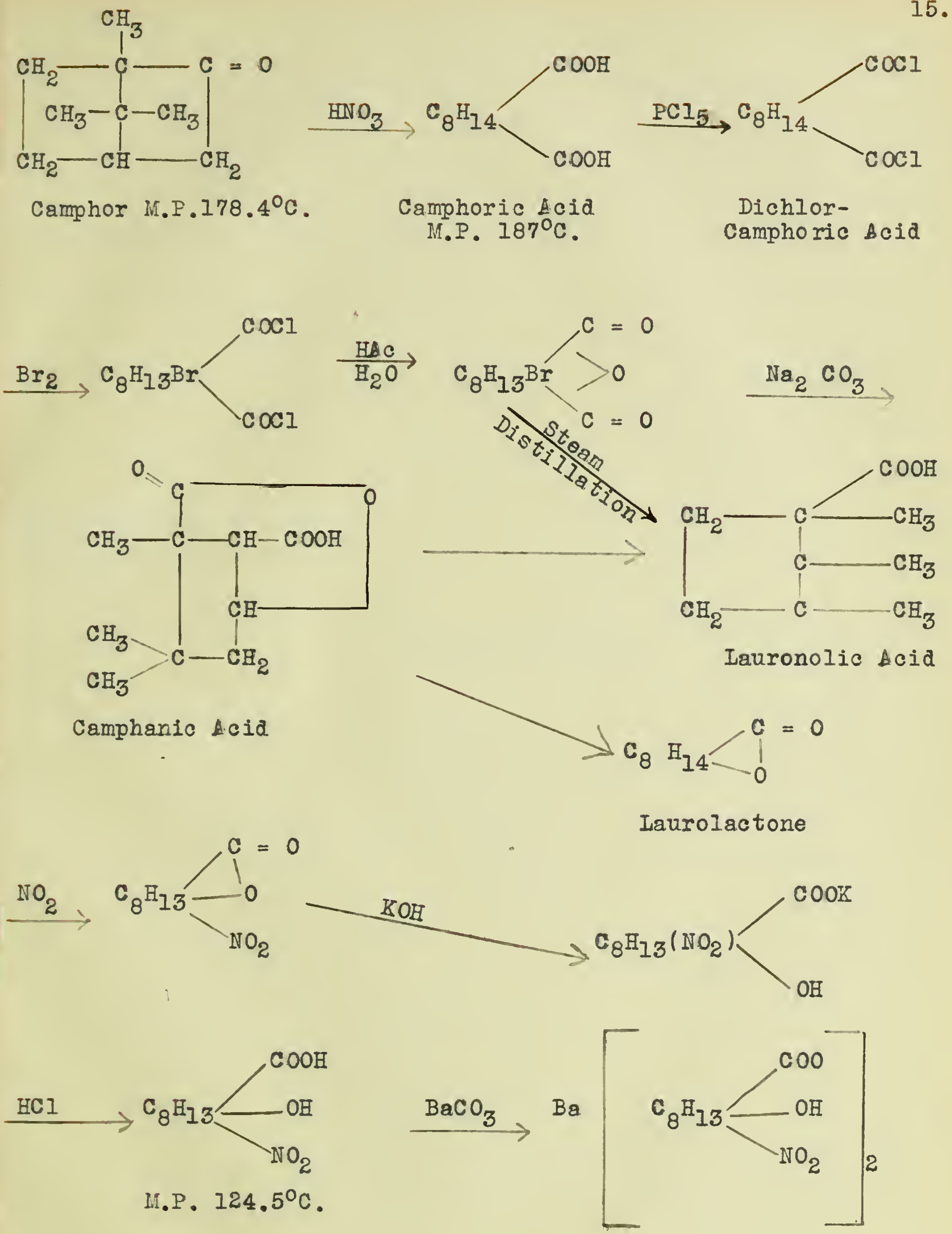


$C_9H_{13}(CO_2H)(OH)(NO_2)$

Calculated -- C = 52.4 H = 6.5 N = 6.11 O = 34.99
Found ---------C = 47.18 H = 6.46 N = 9.55 O = 33.175

These results would give the acid an empirical formula of $C_8H_{12}NO_4$.

The barium salt was prepared by treating the acid with barium carbonate, filtering the excess barium carbonate and evaporating the solution in a dessicator. The salt was then dissolved in hot water and allowed to crystallize by evaporation, finally separating out in fine white needles. Dried in air at 110° for three hours, 0.1 gram lost 0.0022 grams water or 0.022 per cent. Analysis of the dried salt gave 36.09 per cent barium, which if the acid is monobasic, would indicate a molecular weight of 245.13, but if bibasic, the molecular weight will be 122.56.



Camphor M.P.178.4°C.

Camphoric Acid M.P. 187°C.

Dichlor-Camphoric Acid

Camphanic Acid

Lauronolic Acid

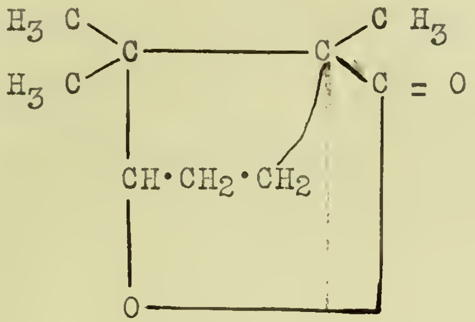
Laurolactone

M.P. 124.5°C.

ISOCAMPHOLACTONE.

ISOCAMPHOLACTONE.

Isocampholactone melts at 32-33°, and boils at 123.4°, at 28 mm. The following formula has been assigned to it,



A mixture of 3.5 cc. concentrated nitric acid and 5.5 cc. concentrated sulphuric acid, cooled in a freezing mixture was added to one gram of the isolactone. After complete solution it was poured onto snow and finally extracted with ether. After evaporation of the ether the residue was again nitrated, using double the amount of acids used in the first case. After standing over night, it was again extracted with ether, which on evaporation left 0.6 gram residue. No crystalline product resulted from this nitration. If not kept in a freezing mixture the action is very violent and a large volume of NO_2 is formed. Further attempts at nitration gave better results, using nitric acid of varying specific gravities. One gram of isocampholactone used in each case gave the following results:

5 cc. cold HNO_3 (Sp.Gr.1.42) gave no crystalline product.
5 cc. HNO_3 (1.27) heated on steam bath over night 0.55 gram isonitrocampholactone.
5 cc. HNO_3 (1.42) heated 3.5 hours gave only a few crystals.
5 cc. (1.22) heated 2.5 days gave .4516 grams melting at 110°.
5 cc. (1.27) heated 2.5 days gave .5475 grams melting at 116°.
5 cc. (1.32) heated 2.5 days gave .5970 grams melting at 117°.

The nitration was carried out in a long glass tube sealed at one end with a loosely fitting stopper in the form of a test tube. After nitration the solution was poured into water and the nitroisocampholactone separated in flaky crystals. Crystallizing from ligroin gives it a melting point of 122°C.

Aminoisocampholactone[19] has been prepared by treating nitroisocampholactone with tin and hydrochloric acid. This compound melts at 84°, crystallizing in small indefinite crystals.

The attempt to prepare this amino derivative was unsuccessful. Two grams of the nitroisocampholactone were treated with tin and HCl and extracted with ether. After purifying the residue it was again dissolved in absolute ether and exposed to dry HCl gas forming a small amount of white solid material. The hydrochloride was dissolved in water in a separatory funnel and ether added. Then a few drops of potassium carbonate solution at a time are added, followed by extraction with ether. After evaporation of the ether the residue melted at 122° in each case, showing that no reduction has taken place. In each case an oily brown product was formed where the amino compound should have separated out, giving evidence of probable decomposition.

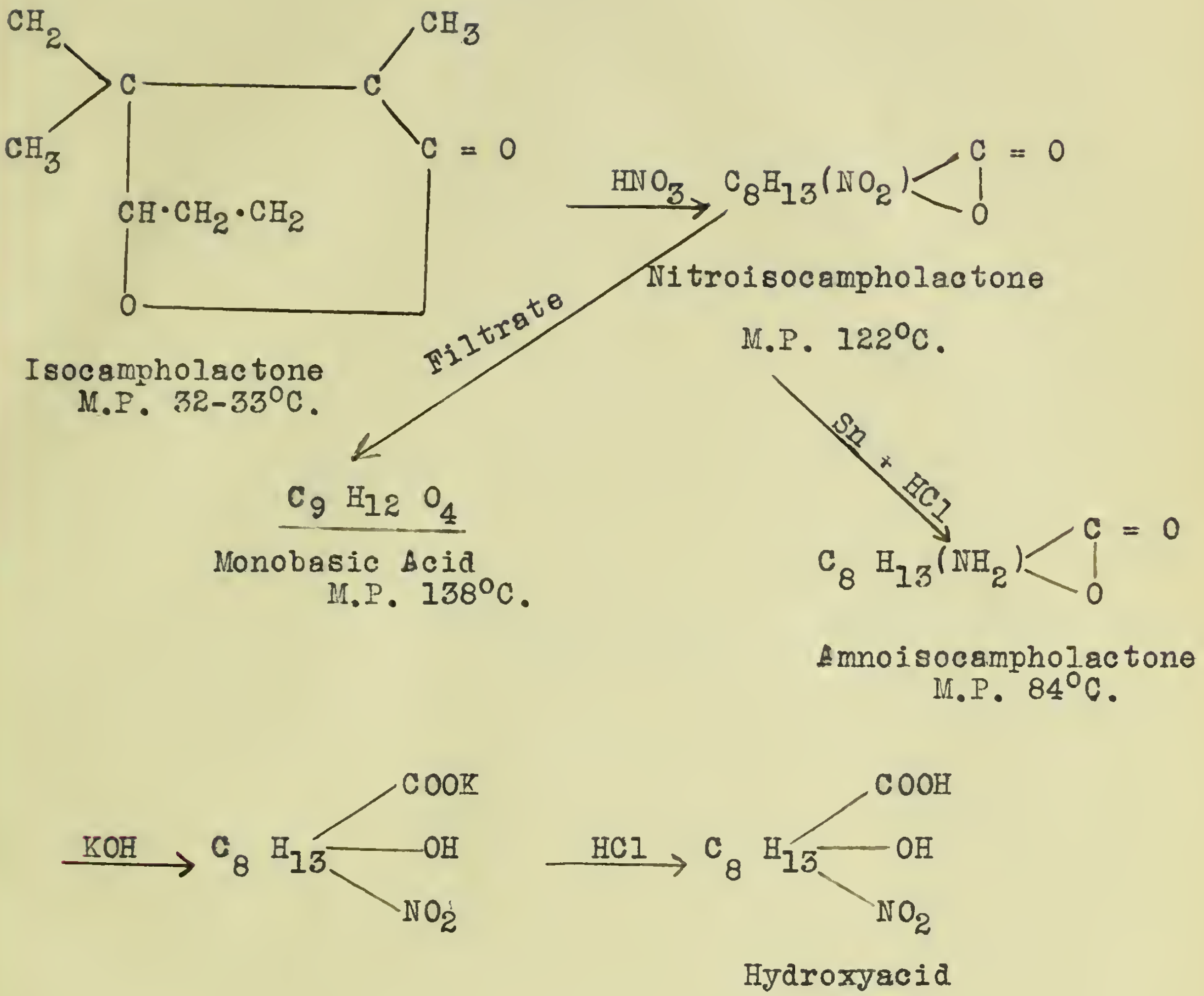
The solution from which the nitroisocampholactone was precipitated, yields a pale yellow, oily substance on evaporation, which crystallizes on standing three or four days. After drying on a porous plate to remove the oily portion the residue was crystallized from benzene and absolute alcohol. This substance gives an acid reaction, and melts at 138°, and has a specific rotation at 31.5° of -50.39[20] for 0.1270 grams in 5 cc. absolute alcohol.

Titration with standard alkali has given this acid a

molecular weight of 186 for a monobasic acid ($C_9 H_{12} O_4$ --184).

Half a gram of this acid was placed in a test tube with a loosely fitting stopper, with 2.5 moles KOH and heated for 24 hours on the steam bath. After cooling with ice a slight excess over the calculated amount of HCl was added and the solution extracted with ether. The residue after evaporation of the ether melts at 139° proving that no change has taken place.

Another portion of 0.5 gram of this acid was treated with N/10 KOH until neutral, using the spot test with methyl red as indicator, so as not to get any of the coloring matter into the acid. After neutralization, a slight excess of nitric acid was added and then an excess of silver nitrate solution. This operation was carried out with the intention of finding out whether the acid was bibasic or monobasic, but no precipitate was formed on the addition of $AgNO_3$, due to the solubility of the silver salt water. 10% NaOH, after heating 24 hours, gave a heavy white ppt. on addition of $AgNO_3$ solution.


Isocampholactone
M.P. 32-33°C.
HNO3
C8H13(NO2) C = O O
Nitroisocampholactone
M.P. 122°C.
Filtrate
C9 H12 O4
Monobasic Acid
M.P. 138°C.
Sn + HCl
C8 H13(NH2) C = O O
Amnoisocampholactone
M.P. 84°C.
KOH
C8 H13 COOK OH NO2
HCl
C8 H13 COOH OH NO2
Hydroxyacid

CAMPHANIC ACID.

CAMPHANIC ACID.

The remainder of this investigation has been devoted to an attempt to prepare an hydroxy acid, starting with camphanic acid as the basis.

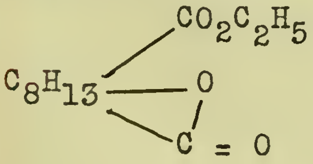
Eleven grams of camphanic acid were heated on the water bath with 45 cc. of a 10 per cent NaOH solution, for 24 hours. The excess NaOH was titrated with dilute nitric acid using the phenolphthalein spot test to determine the end point. An excess of $AgNO_3$ was then added and the precipitate filtered and thoroughly dried. The silver salt was then treated with a slight excess over one mole of ethyl iodide in an ether solution, and heated in a reflux condenser on the steam bath for 3 or 4 hours, after which the ester is extracted with ether, dried over Na_2SO_4, and the ether evaporated.

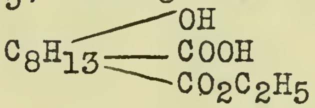
The ester[21] is then taken up with absolute alcohol, and treated with a slight excess over one mole of 30 per cent NaOH solution, finally boiling for 3 hours. As no precipitate formed on adding a drop of this solution to HCl or water, the heating was continued over night, after which a white precipitate formed on pouring into HCl, but none formed on pouring into water. This was evidently NaCl, and it gave the characteristic chloride test. After the removal of this precipitate a small amount of substance crystallized from the acid solution on standing. This has a melting point of 187.5°. Extraction with ether gave a small amount of residue melting at 187°. Re-crystallization from ether gives this substance a melting point of 192°, and it must be unchanged camphanic acid. It follows from this result that saponification takes place very readily and no heat is necessary. Consequently, another amount of the ester was formed in the same manner but this time instead of warming

the solution it was cooled to 0°, and maintained at this temperature for half an hour before the addition of the NaOH solution, after which it was allowed to remain at that temperature for another half hour.

The alcohol was then evaporated under diminished pressure at 30°, and the residue extracted with ether, Only a small amount of material was removed at this point, having an odor of iodoform. The original solution was acidified with HCl and again extracted with ether, leaving on evaporation an oily liquid which does not crystallize after standing a week in a vacuum dessicator.

Treatment of this oily liquid with a 10% solution of Na_2CO_3 and extracting with ether gives a white crystalline product melting at 57°. Since this product is formed by the addition of Na_2CO_3, it cannot be an hydroxy acid, but rather a lactone. From the method of synthesizing this lactone it has the formula,- $C_8H_{13}(CO_2)CO_2C_2H_5$, while the formula for the acid would be, $C_8H_{13}(OH)CO_2H\cdot CO_2C_2H_5$, having the following composition:





	C	H	O
Acid -------	59.01 %	8.19 %	32.8 %
Lactone ----	63.7	8.0	28.3
Analysis ---	65.4	8.13	26.47

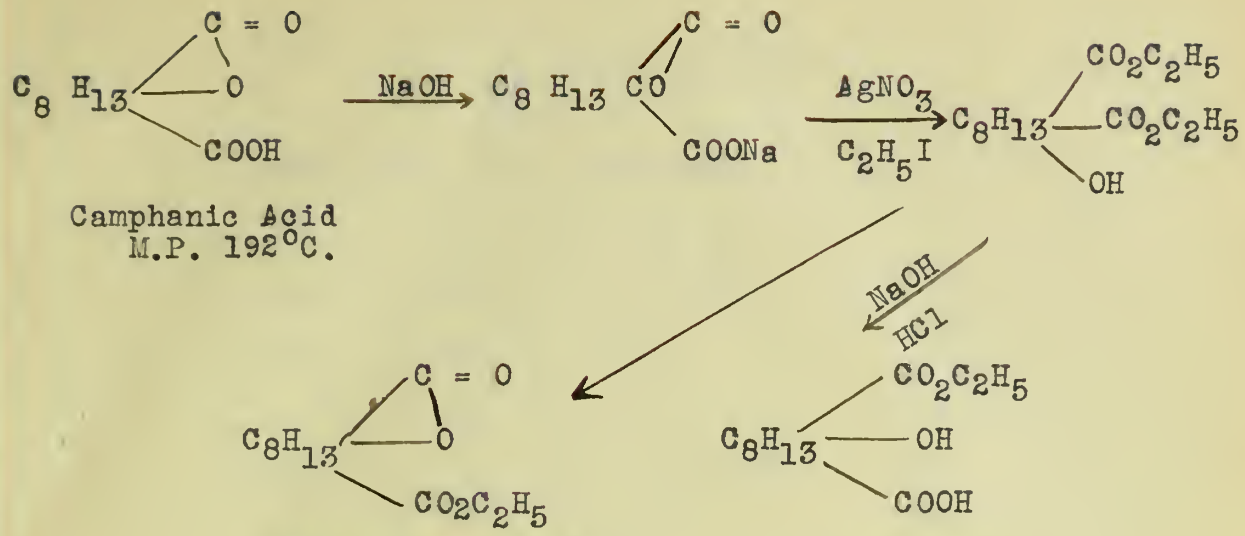
The analysis agrees most closely with the formula assigned to the lactone.

Six grams of the diethyl ester were treated with NaOH as before. When the alcohol had been removed and the residue extracted with ether as before, instead of getting a small amount of CHI_3, an oily liquid was obtained which crystallized in long needles on stand-

ing half an hour in a vacuum. After crystallizing from ligroin, it melts at 53°. This may be the ester of camphanic acid[22], which has the formula $C_8H_{13}(CO_2)CO_2C_2H_5$, and melts at 63° [23]. The remaining portion was acidified with HCl and again extracted with ether, removing a small amount of liquid as before. This, on treatment with Na_2CO_3 as before, yielded a white crystalline lactone melting at 57°.

A mixture of the ester of camphanic acid and the above compound melts at 60°C. According to Auwers and Schnell[23] the ester melts at 62°; Wreden gives the melting point as 63°, and Rudzinski[22] states 58° as the M,P.

This substance then must be camphanic ester and not a lactone as expected.



Camphanic Acid
M.P. 192°C.

Lactone M.P. 57°C.

M.P. 53°C.

Hydroxyacid.

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